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Process for the conversion of clefins having from 4 to 12 carbon atoms to propylene.

(a) A process for the conversion of olefins having from 4 to 12 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder), selected from silicalites, boralites, chromosilicates and those zeolites ZSM5 and ZSM11 in which SiO₂/Al₂O₃ (by moles) is > 350, at a space velocity of from 5 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and at a temperature of from 400 to 600°C, said zeolitic compound being used as such or in a modified form.

PROCESS FOR THE CONVERSION OF OLEFINS HAVING FROM 4 TO 12 CARBON ATOMS TO PROPYLENE

The invention concerns a process for the conversion of olefins having from 4 to 12 carbon atoms into propylene. Nowadays huge amounts of olefine cuts, from C₄ to C₁₂, linear or branched, are available throughout the world and they are widely employed for different purposes, such as described for instance in Italian patent publications 24152 A/82, 24550 A/82 and 19292 A/83. Sometimes, however, because of contingent reasons, even outside the chemical field, like for instance transportation difficulties, it would be better to have still further possibilities of use. A promising use of said olefins would be their conversion into propylene and/or ethylene.

However, endurance tests have shown that the excellent initial behavior of some catalysts, like for instance ZSM5 and ZSM11, disappears after some time; after a few weeks conversion and selectivity drop to poor levels.

An object of the invention is to provide a process for catalytically converting olefin cuts $\mathbf{C_4}^-$ - $\mathbf{C_{12}}^-$ with high propylene (and optionally also ethylene) yields and with a long life time of the catalyst before substitution or regeneration.

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In its most general form, the invention concerns a process for the conversion of olefins having from 4 to 12 carbon atoms into propylene which is characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder) selected from silicalites, boralites, chromosilicates and those zeolites ZSM5 and ZSM11 in which SiO₂/Al₂O₃ (by moles) is >350, at a space velocity of from 5 to 200 kg/h of olefins per kg of pure zeolitic compound, binder excluded, and at a temperature of from 400 to 600°C, said zeolitic compound being used as such or in a modified form.

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The behavior of silicalites depends on the conversion pressure; for instance, if the silicalite is silicalite-1 and if the pressure is substantially atmospheric, the space velocity must be lower than 50 h^{-1} ; if said compound is silicalite-1 and if the pressure is from 1.5 to 7.5 absolute atmospheres the space velocity must be in general above 50 h^{-1} .

Best results are obtained when said catalytic silicalite-1 is activated in the conversion reaction of the olefins into propylene, under said operative conditions. This initial (activating) run takes at least 8 and preferably 12 hours; the silicalite-1 is used as such or in a modified form and the modifying element is selected from Cr, Mg, Ca, Sr and Ba.

The modifying element can be incorporated into the catalyst by means of ion exchange or by any other method, for instance impregnation or co-precipitation during the synthesis of the zeolitic compound.

According to a particularly advantageous way for the preparation of a non-modified silicalite, the raw product coming from the zeolite synthesis is dried, for instance at 120°C, calcined (e.g. at 540°C for some hours), in order to remove all the residual organic templating agent, and then exchanged with an aqueous solution of HCl, NH₄Cl, NH₄NO₃ or an equivalent H⁺ or NH₄ source. When an ammonium compound is used, it is necessary to heat, e.g. at 400°C, in order to obtain the acid form of the silicate. A survey of techniques alternative to ion exchange is given e.g. in U.S. patents 3,140,249; 3,140,251; 3,140,253 and in European patent publications 30796, 36707, 37168, 40463, 68754.

The zeolitic material, after calcination and conversion into the acid form, shows a long endurance and a very high catalytic activity. These zeolitic compounds can be used as catalysts (as such or in a modified form) optionally in admixture with suitable amounts of binders, for instance SiO₂ or Al₂O₃. A list of other binders can be found

e.g. in European patent publication 36707. The regeneration can be carried out in air for some hours, at 400-600°C. A steam regeneration is described in European patent publication 36704 and according to a further and very successful method, the catalyst can be regenerated by a hydrogen treatment.

As to the initial activation of the catalyst, some methods are described in European patent publications 34444 and 35830; in general it is advisable to activate the catalyst for some hours in air, at 450-750°C (preferably 540-700°C). Furthermore the conversion itself (of olefins to propylene) has an activating effect on the zeolitic catalyst. In other words, catalyst and reaction affect each other in a mutual, reciprocal and beneficial activating reaction.

Any process for the conversion of more or less heavy olefinic cuts into propylene will be indicated hereafter, as a "post-pyrolysis" process. When the feed of a postpyrolysis process is a mixture of olefins having 4 C atoms, there is a considerable problem to be solved, because the C4 cuts always contain substantial amounts of paraffins, in general, also having 4 C atoms, which paraffins pass the zeolitic bed without taking part in (at 400-600°C) any reaction. Furthermore a small amount of C_A paraffins is produced by the post-pyrolysis process itself. The conversion to C_3H_6 could be enhanced by a recycle of the nonreacted C_4^- olefins or of the C_4^- olefins formed during the reaction. In such a case, however, an increasing accumulation of n-butane and of isobutane would take place. This drawback could be avoided by a separation of paraffins feeding the reactor but such a from olefins before separation is rather difficult. Butenes and isobutane cannot be isolated by a simple distillation and it is usually necessary to carry out an extractive distillation (a complicated technique), which is particularly burdensome for the C_{4}^{-} cuts coming from catalytic cracking, where butane and isobutane may account for even 50% of the whole. The problem, however, can be solved in a surprisingly easy way

by the process according to the invention, when employing an integrated oligomerization step. In other words, a particular embodiment of the invention (the feed being a paraffin-olefin mixture) comprises the following steps (reference is made also to figure 2):

- a) preliminary oligomerization of a $(C_4^- + C_4^+)$ mixture at a temperature of from 320 to 380°C using a catalyst bed of zeolitic nature(see e.g. U.S. patent 4,150,062) to obtain a mixture of olefins having from 5 to 8 C atoms, with the C_4^+ paraffins remaining unconverted;
- b) cooling and condensation of the oligomerization effluent in order to separate the C₄⁺ paraffins as a gaseous phase, and conversion of the remaining (C₅⁻ -C₈⁻) mixture to propylene under typical "post-pyrolysis" operative conditions;
- c) cooling of the effluent from the reactor for the conversion to propylene and compression of said effluent, preferably at 13-16 absolute Kg/cm², whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.

These hydrocarbons ($\langle C_4 \rangle$) can be advantageously recycled to a conventional battery of distillation columns for thermal or catalytic cracking, in order to recover all the propylene contained therein. The small and possible amounts of aromatics (BTX) can be easily separated from the other C_4 hydrocarbons and recycled together with the final $(C_4 - C_8)$ mixture, containing small amounts of butanes produced during the conversion reaction described under item (b) above.

In order to carry out the oligomerization, C_4 olefins, containing C_4 paraffins in any proportion, are initially brought into contact with a catalyst of zeolitic nature, for instance ZSM5 or ZSM11, in an acid or in a modified form, at 250-400°C (preferably 320-380°C) and at space

velocities from 2 to 10 (preferably 4 - 8) kg/h of reactants per kg of pure zeolite (binder excluded). In other words, the olefins of the $(C_4^- + C_4^+)$ mixture are converted almost totally into a $(C_5^- - C_8^-)$ olefinic mixture, while butane and isobutane do not react. The separation of the butanes can thus be carried out very easily by simple cooling with water at room temperature. The olefinic $(C_5^- - C_8^-)$ mixture liquifies while the butanes are separated as a gaseous phase, said $(C_5^- - C_8^-)$ mixtures being optimal raw-materials for the production of propylene.

Depending on the operative conditions of the synthesis of the silicalite, as e.g. the dilution of the starting solutions, the resulting crystallites may have a widely variable size. The crystallites to be employed in the process according to the invention should have, in general, rather small sizes, such small sizes being obtainable, for instance, following the teachings of U.S. patent 3,926,782. The following examples are given merely for illustration purposes and do not in any way limit the scope of the in vention.

OPERATIVE CONDITIONS COMMON TO ALL EXAMPLES

As to the method of preparation of the catalysts see:

- for silicalite-1: U.S. patent 4,061,724;
- for boralite: Taramasso et al.: "Molecular Sieve Borosi-licates", Proc. 5th Int. Conf. on Zeolites, Naples 1980, pages 40-48 (Heyden and Son Ltd. London 1980); the boralite used in the examples has a ratio SiO₂: B₂O₃ of 7
 - (by moles); a more recent method for obtaining boro-silicates is described in European patent publication 77946.
- for chromosilicates: Italian patent publication 22568 A/82, in the name of the Applicant; the chromosilicate used in the examples has a ratio SiO_2 : Cr_2O_3 of 38 (by moles).

As to zeolites ZSM5 showing a very high ${\rm SiO}_2$: ${\rm Al}_2{\rm O}_3$ ratio, not exemplified, see Italian patent publication 21699 A/83, in the name of the Applicant. In the absence of different indications, all the catalysts were activated 2 hours at 540°C before being used.

EXAMPLES 1-6

3 g of zeolitic catalyst, in admixture with 0.9 g of SiO₂ (as a binder), were loaded into a microreactor which was continuously fed, at a pressure slightly above atmospheric pressure with a 50/50 mixture of butene-2-trans and butene-2-cis. Operative conditions and results are given in Table 1.

10 EXAMPLE 7

Example 4 was repeated using a silicalite-1 impregnated with a chromium salt, thus obtaining slightly better results.

EXAMPLES 8-15

0.5 g of zeolitic catalyst, in admixture with 0.21 g of Al₂O₃ (as a binder), were loaded into a microreactor which was continuously fed, at a pressure slightly above the atmospheric pressure with a 70/100 mixture of n-pentene and of helium (by moles). Detailed operative conditions and results are given in Table 2. When modified zeolitic catalysts were used, the modifying element was added by means of impregnation.

EXAMPLES 16-23

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Examples 8 and 9 were repeated replacing pentene with n-hexene (ex. 16 and 17), with 2-methyl-pentene-1 (ex. 18, 19 and 20) and with n-octene-1 (ex. 21, 22 and 23), respectively, the parameters being slightly modified as indicated in Table 3, which shows also the very good results.

EXAMPLES 24-29

2.12 g of zeolitic catalyst were loaded into a micro-reactor which was continuously fed whith 7.5 kg/h of iso-butene per kg of zeolitic catalyst at 550°C and at a pressure slightly above atmospheric pressure. Data and results are given in Table 4.

EXAMPLES 30 AND 31

Examples 24 and 25 were repeated raising the pressure to 5 absolute atmospheres and the space velocity (WHSV) from 7.5 to 45 h^{-1} , thus obtaining analogous results.

EXAMPLES 32-35

and the results are given in Table 5. The results show clearly that a slight increase in pressure, corresponding approximately to the pressure of the olefins in the industrial manufacturing plants, allows the same conversions and selectivities, but at a much higher velocity. In other words, it is surprising and was quite unexpected that a suitable increase of the olefore the output of the industrial plants.

EXAMPLE 36

50 parts by weight of silicalite-1 were admixed with 50 parts of Al₂O₃ (binder) and the mixture was loaded into a microreactor which was continuously fed at atmospheric pressure, with a 50/50 mixture of butene-2-trans and butene-2-cis, at 550°C and at a space velocity of 20 kg/h of olefins per kg of silicalite (binder excluded). The run was very long (120 h) and the results, hour by hour, were continuously monitored and plotted in figure 1. It is worthwhile to note that the initial decrease of conversion is reversed after a few hours; thus the conversion of the olefins itself is likely to be a stimulating activation for the catalyst. In other words, catalyst and reaction effect each other by a mutual and beneficial activating action.

EXAMPLE 37

Example 36 was repeated by using a mixture 65% b.w. silicate-1 + 35% b.w. ${\rm Al}_2{\rm O}_3$ and by raising the space velocity to 67 h⁻¹. In this case, the conversion initially decreased and then the phenomenon was reversed.

5						-				T					T			7
		9		See Ex. 5		F	=	=	9		72.25	40.46	23.65	7.85	30.82	4.77	0.31	
10		S		Chromosilicate	(P)	see Ex. 1		=	.		29.75	34.07	29.73	19.88	32.29	3.46	0.45	
		7		See Ex. 3	÷	=	=	5	7 %		77.06	13.47	£ 0.39	45.13	31.75	5.45	2.95	
15		3		Silicalite-1	8	see Ex. 1	=	=	 		61.95	15.26	44.79	49.23	28.15	6.85	4.95	
20	TABLE	2		see Ex. 1	=	=	=	=	ر دی		29.01	40.40	24.90	18.94	31.73	2.55	0.43	
0.5		-		Boralite	(P)	3 grams (c)	200	۰	<u>-</u>		45.95	29.79	28,36	25.72	38.76	2.51	0.57	
25		EXAMPLE	Operative conditions:		o (moles)	Amount of catalyst	(၁۰)	Space velocity (m)	Data survey after:	(xb.w.)	. lon	Selectivity to iso-C_	vity to C	Vield (iso [+ C])	Sel. to compoundsying Sel. to saturated	797 Sp	Selectivity to C ₂	
30		EX	Operati	Catalyst	S10,/A1	Amount	.Temp. (°C)	Space v	Data su	Results (%b.w.	Conversion	Se lecti	Selecti	Yield (Sel. to	Compounds & C	Selecti	

(a) WHSV (Weight Hourly Space Velocity) namely Kg/h of olefine per Kg. of pure satalyst (binder excluded); (b) SiO,:B,O, = 7 (by moles);

0	1	n	a	n	$\boldsymbol{\mathcal{L}}$	n
U	ı	U	J	U	O	U
_	•	_	_	_	_	_

											-	9	-						0 ′
	• . 15	(*)	See Ex. 14	s	£	=	=	۴ م		60.92	19.63	39.71	36.15	0.76	28.37	1.88	90.9	3.69	
5	71	(*)	Cr-Silicalite	8	See Ex. 8	= ,	=	 		69.22	20.51	34.25	37.90	0.91	29.31	1.21	7.79	6.02	
10	13		See Ex. 12	=	=	8	=	ب ج		10.04	17.92	. 29.52	4.77	0.79	30.38	0.29	4.58	7.27	
	12		Chromosilicate	(¥)	See Ex. 8	E	s .	4.		16.80	21.25	32.50	9.03	0.65	26.90	0.29	7.97	10.83	
15 5 18 Y L	11		See Ex. 10	=	E .	s .	=	e h		19.52	27.97	38.93	13.06	0.31	24.70	0.25	1.79	5.79	
20	10		Boralite	(P)	See Ex. 8	=	*	<u>.</u>		42.81	23.43	39.27	25.84	94.0	27.61	0.58	3.59	4.95	
	6		See Ex. 1	=	=	=	=	4 9		57.00	19.80	39.42	33.76	0.70	29.42	0.84	5.96	3.82	
25	8		Silicalite-1	8	(2)	550	7.14	<u>-</u>		64,26			35.93	96.0	29.27	1.36	6.65	3.06	
30	EXAMPLE	Operative Conditions:	Catalyst	Sio_/Al_O_(moles)	Amount of catalyst	Temp. (°C)	Space velocity (a)	Data survey after:	Results (% b.u.)	Conversion	Selectivity to C.	Selectivity to 6	$\begin{cases} rield (C_2 + C_3) \end{cases}$	compounds < C.	Sel. to C.	Sel. to C	Sel. to BTX (b)	Sel. to others	-) -0

(a) See ex. 1;(b) BIX = benzene + toluene + xylenes; (c) 0.5 g of pure zeolite + 0.21 g of Al₂ g (binder); (d) SiO₂/8₂ g = 7 (by moles); (K) SiO : ${\rm Cr}_2$ 0 = 38 (by moles). (*) Silicalite-1 containing 0.1% b.w. Cr. added by means of impregnation.

						******			-	10) -	-					C	110	19060
-	23	(##)	See Ex. 21	= =	009	7.14	7 h		95.50	16.64	27.56	42.21	0.34	24.37	0.30	21.97	79*5	3.14	n-octene-1
5	22	(***)	See Ex. 21	= =	=	=	6 h		97.47	7.60	33.13	37.75	77.0	28.21	0.65	27.08	2.05	2.77	(***) Feed = n-octene-1
10	21	(***)	See Ex. 16	= E	=	=	1 h		100	9.16	31.64	40.80	0.62	26.96	1.06	24.14	2.66	3.74	hyl-pentene-1;
	20	(#)	See Ex. 18	: :	=	=	7 h		69.6	7.48	55.35	26.48	0.20	11.92	0.00	20.67	0.99	3.26	(**) Feed = 2-methyl-pentene-1;
15 3 1	19	(**)	See Ex. 18	= =	=	E	4 9 ·		97.36	9.29	53.79	61.41	0.41	13.65	0.13	16.54	2.76	3.40	
20	18	(#)	See Ex. 16	= =	=	=	1 h		97.79	10.55	53.03	52.17	0.60	16.78	0.30	13.82	1.89	2.97	+ mylenes ; (*) Feed = n-hexene-1;
	17	(*)	See Ex. 16	= =	=	=	6 th		96.83	9-12	52.90	60.09	0.65	14.80	0.23	17.85	2.22	2.51	
25	16	(*)	Silicalite-1	See Ex.	550	7.14	1 h		98.01	10.38	51.14	82-09	0.78	17.55	0.41	14.64	. 2.81	2.20	- benzene + to
30	EXANPLE	Operative Conditions:	Catalyst	S10 /AL 0 (moles) Amount: of catalyst	Temp. (°C)	Space velocity (a)	Data survey after:	Results (% b.w.)	Conversion	Selectivity to C_	Selectivity to C_	rield $(c_2 + c_3)$	Sel. to saturated compounds < C.	Sel. to C. 4	Sel. to C	Sel. to BIX (b)	Sel.to C	Sel to others	(a) See ex. 1:(b) BTX = benzene + toluene

30	2.5	20	15		10	5	
		TABLE	E 4				
EXAMPLE	57	25	26	72	28	29	
Derative conditions:							
Catalyst	Silicalite-1	See Ex. 24	Boralite	See Ex. 26	Chromosilicate	See Ex. 28	_
Sin_/Al_D (moles)	8	=	(a)	=	<u>e</u>	=	
Amount of catalyst	2.12 g	=	See Ex. 24	=	See Ex. 24	=	
Temp. (°C)	. 055	=	. 550	=	550	s	
Space velocity (h)	7.5	=	7.5	=	7.5	E.	
Date survey after:	£	.e •	1 4	ب ب	e 	æ	
Results (% bow.)				-			
Conversion	81.8	77.3	77.4	62.4	44.5	18.1	
Selectivity to C_	8.47	40.8	39.1	24.8	16.5	12.4	
Yield (C_)	36.0	31.5	30.3	15.è	7.4	2.2	
Sel. to C	4.2	2.6	3.4	1.2	9.0	0.5	
Sel to saturated	e.5	5.6	5.7	2.9	5.1	9.6	
corpounds <c< td=""><td></td><td></td><td></td><td></td><td></td><td>~~</td><td></td></c<>						~~	
Sel to compounds > C	6.4	7.0	7.8	5.4	13.7	8.1	
Sel to linear butenes	35.1	0.44	6.0	65.7	63.9	75.1	
(x (x 0 x 0 x 0 x 0 x 0 x 0 x 0 x 0 x	1 (4) (5)	96 - 0 - 3 - 3					

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•	35	(#)	See Ex. 34	5	E	=	=	.E		67.32	26.00	17.50	3.20	8.40		72.60	16.50	
15 	34	(*	See Ex. 32	=	=	280	09	<u>۔</u>		79.31	39.66	31.45	4.21	14.14		27.80	14.19	
⊒ . 8 ¥ 20 ⊢	33	(*)	See Ex. 32	=	=	=	=	æ æ		73.80	39.89	29.44	3.19	10.62		25.73	20.58	
	32	(*)	Silicalite-1	8	о О	570	90	<u> </u>		82.24	31.98	26.33	3.89	13.35		36.02	14.76	
25	37	Operative conditions:		(moles)	catalyst	•	city (h-1)	y after:	b.w.)		, to C	V 2	j	Sel. to saturated compounds		Sel. to compounds C.	obutene	
30	EXAMPLE	Operative	Catalyst	Si0 /A1 0	Amount of catalyst	Temp. (°C)	Space velocity (h)	Data survey after:	Results (% b.w.	Canyersion	Selectivity to C	Yield (C_)	Sel. to C.	Sel, to sate	ಳ	Sel. to con	Sel. to isobutene	

(*) Pressure = 6 absolute atmospheres;

(**) Pressure = 9 absolute atmospheres.

CLAIMS

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- 1. A process for the conversion of olefins having from 4 to 12 carbon atoms to propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder), selected from silicalites, boralites, chromosilicates and those zeolites ZSM5 and ZSM1l in which SiO₂/Al₂O₃ (by moles) is > 350, at a space velocity of from 5 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and at a temperature of from 400 to 600°C, said zeolitic compound being used as such or in a modified form.
 - 2. The process of claim 1, wherein said compound is silicalite-1, the pressure is substantially atmospheric and the space velocity is from 5 to 50 h⁻¹.
 - 3. The process of claim 1, wherein said compound is silicalite-1, the pressure is from 1.5 to 7.5 absolute atmospheres and the space velocity is from 50 to 200 $\rm h^{-1}$
- 4. The process of any of claims 1-3, wherein said compound is silicalite-1 which is activated in the conversion reaction of said olefins to propylene, under the operative conditions of claim 1, the initial (activating) run being carried out at least 8 and preferably 12 hours.
 - 5. The process of any of claims 1-4, wherein said olefins are selected from isobutene and linear butenes and wherein said binder is SiO₂.
- 35 6. The process of any of claims 1-4, wherein said olefins contain from 5 to 8 carbon atoms and wherein said binder is Al₂O₃.

- 7. The process of any of claims 1-6, wherein said compound is silicalite-1 in a non-modified form.
- 8. The process of any of claims 1-6, wherein said compound is silicalite-1 in a modified form, the modifying element being Cr, Mg, Ca, Sr or Ba.
- 9. A process for the conversion of olefins having 4 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder) selected from silicalites and those zeolites ZSM5 and ZSM11 in which SiO₂/Al₂O₃ (by moles) is >350, at a pressure of from 1.5 to 7.5 atmospheres, a space velocity of from 50 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and a temperature of from 400 to 600°C, said compound being used as such or in a form modified by an element selected from Cr, Mg, Ca, Sr and Ba.
- 10. A process for the conversion of olefins having from 5 to 8 carbon atoms into propylene, characterized in that said olefins are brought into contact with a zeolitic compound (optionally in admixture with a binder) selected from silicalites and those zeolites ZSM5 and ZSM11 in which SiO₂/Al₂O₃ (by moles) is ≥350, at a pressure of from 1.5 to 7.5 atmospheres, a space velocity of from 50 to 200 kg/h of olefins per kg of pure zeolitic compound (binder excluded) and a temperature of from 400 to 600°C, said compound being used as such or in a form modified by an element selected from Cr, Mg, Ca, Sr and Ba.
- 35 11. The process of claims 9 or 10 wherein said compound is silicalite-1 which is activated in the conversion reaction of said olefins to propylene, under said operative conditions, the initial (activating) run being carried out at least 8 and preferably 12 hours.

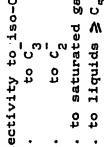
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- 12. A process for the conversion into propylene of mixtures of olefins having 4 C atoms, said mixtures containing also C₄⁺ paraffins that cannot be easily separated from olefins, which process comprises the following steps:
 - a) preliminary oligomerization of a $(C_4^- + C_4^+)$ mixture at a temperature of from 320 to 380°C using a catalyst bed of zeolitic nature to obtain a mixture of olefins having from 5 to 8 C atoms, with the C_4^+ paraffins remaining unconverted;
 - b) cooling and condensation of the oligomerization effluent in order to separate the C_4^+ paraffins as a gaseous phase, and conversion of the remaining $(C_5^- C_8^-)$ mixture to propylene under the typical "post-pyrolysis" reaction conditions of claim 1;
 - c) cooling the effluent from the reactor for the conversion to propylene and compression of said effluent preferably at 13-16 absolute kg/cm², whereby the hydrocarbons having 4 or more C atoms are condensed and the hydrocarbons having less than 4 C atoms are separated as a gaseous phase.



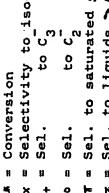
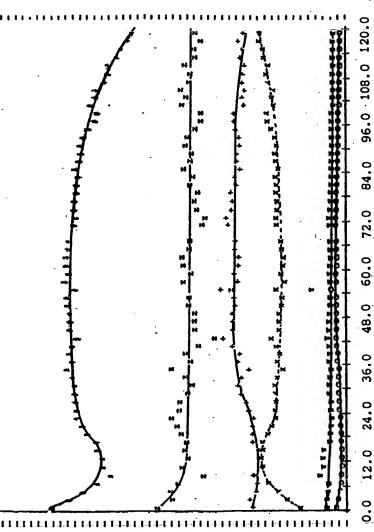
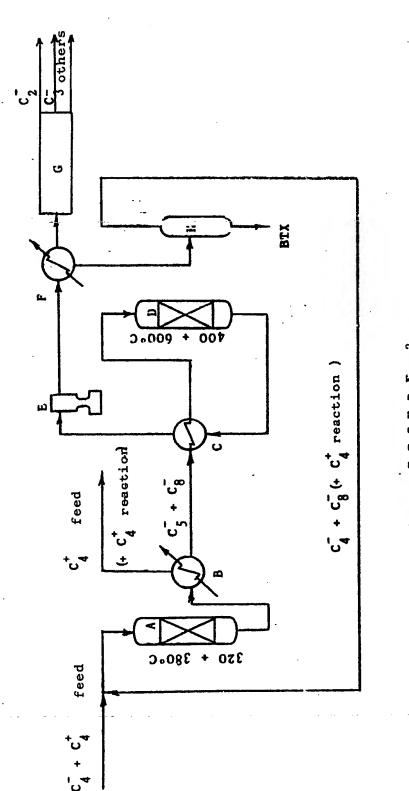


FIGURE 1







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EUROPEAN SEARCH REPORT

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